

The University of Chicago

A PHOTO-ELECTRIC POLARIMETER

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1938

By
FRED KARUSH

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1941

The University of Chicago

A PHOTO-ELECTRIC POLARIMETER

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1938

By
FRED KARUSH

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1941



The author is pleased to express his appreciation to Professor Thorfin R. Hogness for his consistent encouragement and timely aid during the course of the research.

To Dr. Franklin Offner, for his unselfish interest and fruitful advice, the author owes a debt of gratitude.

The writer also wishes to thank Dr. Aaron M. Altschul for assistance in the construction of the polarimeter and Mr. Sam Weissman for many valuable suggestions.



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41533920_0143

Introduction

The advent of the photo-electric cell has stimulated many investigators to attempt to construct photo-electric polarimeters. The purpose of these experiments was to build an instrument which is free from the limitations inherent in visual polariscopes. These consist of the lack of objectivity in determining readings, the fatigue which is imposed on the observer, and insufficient sensitivity for certain purposes.

A photo-electric polarimeter has recently been described which involves the use of a direct current amplifying circuit.¹ In this instrument the azimuths of the polarizer and analyzer are placed at 45° to each other in order to obtain maximum sensitivity. The light which passes through the analyzer is allowed to impinge on the photo-electric cell which is firmly fastened to the same base as the analyzer so that it rotates with it. After the instrument has been calibrated, the optically active medium is placed between the polarizer and analyzer and readings are taken for positions of 45° and -45° . The accuracy of $.01^{\circ}$ which is claimed implies that the light source and amplifier are stable to within 0.02%, conditions which at the present time are not possible.

To make the photo-electric polarimeter independent of fluctuations in the intensity of the light source, an instrument was designed in which the light beam was split into two portions.² One was allowed to pass through a polarizer, optically active medium, and an analyzer which is placed at 45° with respect to the polarizer; the other which is unpolarized passes through the optically active medium. The two beams terminate on two photo-electric cells and the currents are then amplified and oppose each other through some electrical meter. The limitations of this method are the instability of the amplifiers and the fact that the two photo-electric cells do not respond exactly alike to changes in light intensity.

¹D. R. Morey, Rev. Sci. Instruments, 3, 24 (1932).

²Ebert and Kortum, Z. physik Chem., (B) 13, 111 (1931).

A method of measuring optical rotations has been developed recently which is independent of random fluctuations of the light source and employs only one photo-electric cell.^{3,4} The apparatus involves the rotation of either the analyzer or polarizer by a constant speed motor. The zero point is determined by the use of ear-phones or a rectifying device but the noise characteristics of the amplifier limit the accuracy which can be attained. In addition, it has been shown on theoretical grounds that any method of detecting the zero point of the instrument which depends on the intensity of the sound produced or on the rectification of the a.c. output is operating at minimum sensitivity.⁵

The Hardy spectrophotometer⁶ detects the zero point of the instrument by a method which depends linearly on the amplitude of the a.c. output from the amplifier. This involves the task of measuring the phase difference between the output from the amplifier and a constant phase a.c. voltage of exactly the same frequency from another source. Since the spectrophotometer is used at the point at which the phase difference is $\frac{\pi}{2}$, it can easily be shown that the instrument is being operated at maximum sensitivity.

The following pages will be devoted to a detailed description of an a.c. photo-electric polarimeter which operates at maximum sensitivity; it will be shown to have as high an accuracy as any photo-electric polarimeter yet reported. In addition, definite suggestions for the improvement of the apparatus in order to increase the accuracy will be given.

Theoretical Discussion

A diagram of the optical path is presented in Fig. 1. The alternating current which is generated by the photo-electric cell due to the rotation of the polaroid disk is amplified and sent through the moving coil of an electrodynamometer. This instrument consists simply of a moving coil placed within a fixed coil with a separate set of leads for each coil. The axes of the coils are perpendicular to each other. Another a.c. voltage of the same

³Schonrock and Einsporn, Physik. Z., 37 (1936).

⁴Kent and Lawson, J. Optical Soc. Am., 27, 117 (1937).

⁵A. M. Altshul, Ph. D. Dissertation, University of Chicago (1937).

⁶A. C. Hardy, J. Optical Soc. Am., 25, 305 (1935).

Diagram of the Optical Path

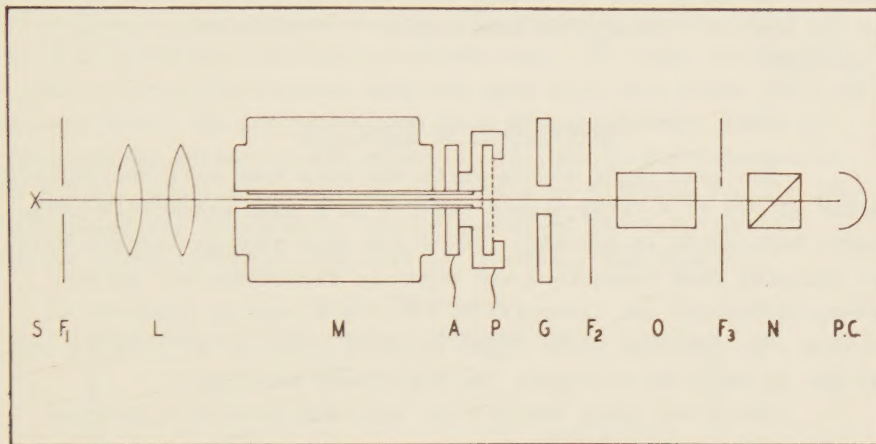


Fig. 1

S, light source; F, stops; L, achromatic collimating lens system; M, constant speed motor with hollow shaft; A, armature on shaft; P, frame which carries rotating polaroid disk; G, shutter; O, solution; N, analyzer; P.C., photo-electric cell.

frequency is induced by the rotation of the armature between the poles of a magnet. This output is also amplified and passes through the fixed coil of the dynamometer.

The torque on the gold fiber supporting the moving coil, which results from the interaction of the magnetic fields, is given by the equation

$$T = K I_f I_m \cos \theta^7$$

where K is a constant depending on the instrument, I_f and I_m are the currents passing through the fixed and moving coils respectively, and θ is the phase angle between the two a.c. inputs. It is easily seen that the rate of change of T with θ is a maximum at $\theta = \frac{\pi}{2}$. The value of θ depends on the position of the analyzer. When an optically active medium is present, the change in θ is exactly equal to the optical rotation of the medium. In the actual operation of the polarimeter θ is maintained approximately equal to $\frac{\pi}{2}$ and the instrument functions at maximum sensitivity. If we can assume that the phase of the a.c. current coming from the

⁷Laws, Electrical Measurements (McGraw-Hill Co., 1917).

photo-electric current amplifier does not vary with a change in the input voltage from the photo-electric cell, and if the dynamometer is being used as a null instrument, then the determination of the optical rotation is independent of fluctuations in light intensity.

Description of Apparatus

The only light source which has been used with the polarimeter as yet is a fifty candle power 6 to 8 volt automobile headlight bulb which is operated from a six volt storage battery which is shielded from electrical and magnetic disturbances. Under these conditions the intensity of the light remains constant to within .3%. Because white light is being used, an achromatic lens system is employed to render the light beam parallel.

The motor which rotates the polaroid disk is a one-hundredth horse-power 1800 R.P.M. synchronous motor with a hollow shaft which permits the light to pass through it. The diameter of the hole is $1/4$ inch. In the course of our work we were faced with the problem of reducing the vibrations of the motor to a minimum, because the slightest movement of the motor would alter the relative position of the polaroid disk with respect to the analyzer and thus change the phase angle. This problem was satisfactorily solved by the following means. The first, was to replace the ball bearings in the motor by carefully machined phosphor bronze sleeve bearings which resulted in a reduction in the amount of vibration. The motor was then bolted to a concrete pier, three feet high and about one foot square which in turn rested on a section of vibrocork two inches thick. The mass of the concrete block, about two hundred pounds, reduced the vibrations of the motor considerably. Finally, it was found that if a resistance is put in series with the motor and only enough voltage drop across the motor to keep it rotating synchronously is permitted, there is a further reduction in the amplitude of the vibrations.

At the front end of the motor a polaroid disk, five cm. in diameter, is carefully mounted in an aluminum frame on the shaft in such a way that the incident light strikes perpendicularly on the surface of the disk. It was found that in the case of commercial polaroid disks the faces were not parallel and the thickness of the plate over different portions of the disk varied by as much as three thousandths of an inch. This resulted in the rotation of

the entire image about the axis of the optical path; thus different portions of the cross-section of the light beam passed through the stops and impinged on the photo-electric cell as the motor rotated. This is undesirable because the intensity of the light beam is not constant over its cross-section. In order to eliminate this, a specially ground polaroid disk with very plane parallel faces was made. As far as we have been able to detect, there is no deleterious effect on the polaroid disk due to its rotation at 1800 R.P.M. Since there are two positions of darkness for the polaroid during one revolution, the frequency of the a.c. current from the photo-electric cell will be 60 cycles per second.

A. C. Generstor

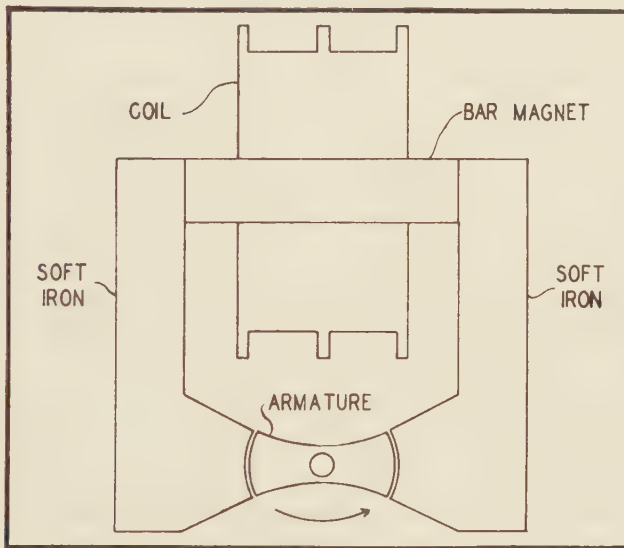


Fig. 2

Situated directly behind the aluminum case and connected to it, is an armature of soft iron about two inches in diameter. This rotates between the poles of a magnet as indicated in Fig. 2. The stationary portion of the generator which is bolted to the same concrete block as the motor consists of a bar magnet over which is placed a coil wound in two adjacent sections on a bakelite spool. Each section has 6720 turns of number 38 copper wire with a resistance of 1750 ohms. Screwed to each side of the magnet is a section of soft iron of such a shape as to give a minimum of air path between the poles of the generator for one position of the

armature and a maximum air path for another position. The change in the strength of the magnetic field in the neighborhood of the coil due to the varying air gap results in an induced voltage in the coil which is then amplified. Since there are two positions for a minimum air gap during one complete rotation of the armature, the induced voltage will have a frequency twice that of the motor, namely, 60 cycles per second. This is exactly the same frequency as the output of the photo-electric cell. It is seen too that any change in the frequency of the motor will result in identical frequency changes in the generator and photo-electric cell outputs. This means that the phase difference between the a.c. voltages will remain constant.

The analyzer, which consists of a nicol prism, a graduated circular disk in which the prism is mounted, and its supporting frame, is part of an old visual polariscope. This portion of the apparatus is bolted to a metal base which in turn is bolted to the floor to prevent any movement of the analyzer.

The circuit which is used to amplify the current from the photo-electric cell is indicated in Fig. 3. The type 38 tube, which is recommended by Neitzert and Johnson,⁸ and the photo-electric cell are contained in a metal can and are shielded from electrical and magnetic disturbances. In addition, they are suspended in cotton to eliminate microphonic disturbances. All the B batteries are placed in one metal box and the storage batteries in another with all the leads from them to the amplifier shielded. The remaining part of the amplifier is contained in another metal can. The type 6C5 tube used in the second stage is a triode selected to give linear amplification and the type 6V6G tube of the last stage serves to furnish a large amount of current for the dynamometer.

To the integral part of the amplifier, has been added a degenerative feed-back circuit, the purpose of which is to reduce greatly all the frequencies except the one for which it is tuned.⁹ In this particular problem, its function was to eliminate as much of the second and higher harmonics as possible. The combination of the condensers C_{16} , C_{17} , C_{18} and the resistors R_{20} , R_{21} , R_{22} comprise a modified Wien bridge in which the values and ratios of the

⁸Neitzert and Johnson, Rev. Sci. Instruments, 5, 126 (1934).

⁹H. H. Scott, Inst. Radio Eng., 26, 226 (1938).

P.C. - Photo-electric cell

R₁ - S.S. White carbon resistor 2×10^8 ohms

R₂ - S.S. White carbon resistor 1×10^8 ohms

R₃ - Carbon resistor 10^6 ohms

R₄ - Carbon resistor 25M ohms

R₅, R₆, R₇, R₈ - Carbon resistor 100 M ohms

R₉ - S.S. White carbon resistor 10^6 ohms

R₁₀ - Carbon resistor 500M ohms

R₁₁ - Carbon resistor 6M ohms

R₁₂ - Carbon resistor 2×10^6 ohms

R₁₃ - Carbon resistor 50M ohms

R₁₄ - Carbon resistor 250 ohms

R₁₅ - Ten watt wire wound resistor 1000 ohms

R₁₆ - Carbon resistor 150 ohms

R₁₇ - Carbon resistor 250M ohms

R₁₈ - Carbon resistor 1.5×10^6 ohms

R₁₉ - Carbon resistor 2M ohms

R₂₀, R₂₁ - S.S. White carbon resistors 90M ohms plus 10M ohms wire wound clarostats

R₂₂ - S.S. White carbon resistor 43M ohms plus 5M ohms wire wound clarostats

P₁ - Logarithmatic carbon potentiometer 2×10^6 ohms

P₂ - Logarithmatic carbon potentiometer 5×10^6 ohms

C₁ - Mica condenser .003 microfarads

C₂, C₃, C₄, C₅, C₆, C₇, - Paper condensers 1 microfarad

C₈ - Electrolytic condenser 25 microfarads

C₉ - Paper condenser .02 microfarads

C₁₀ - Paper condenser .00025 microfarads

C₁₁ - Electrolytic condenser 8-8-18-18 microfarads

C₁₂, C₁₃ - Paper condensers .1 microfarad

C₁₄ - Paper condenser .01 microfarad

C₁₅ - Electrolytic condenser 50 microfarads

C₁₆ - Paper condenser .0485 microfarads plus variable trimmer condenser 560 to 940 micromicrofarads

C₁₇, C₁₈ - Paper condenser .0245 microfarads plus variable trimmer condenser 560 to 940 micromicrofarads

F - Fuse .1 ampere

S - Switch

M - Moving coil of electrodynamometer

Amplifier Circuit for Photo-electric Current

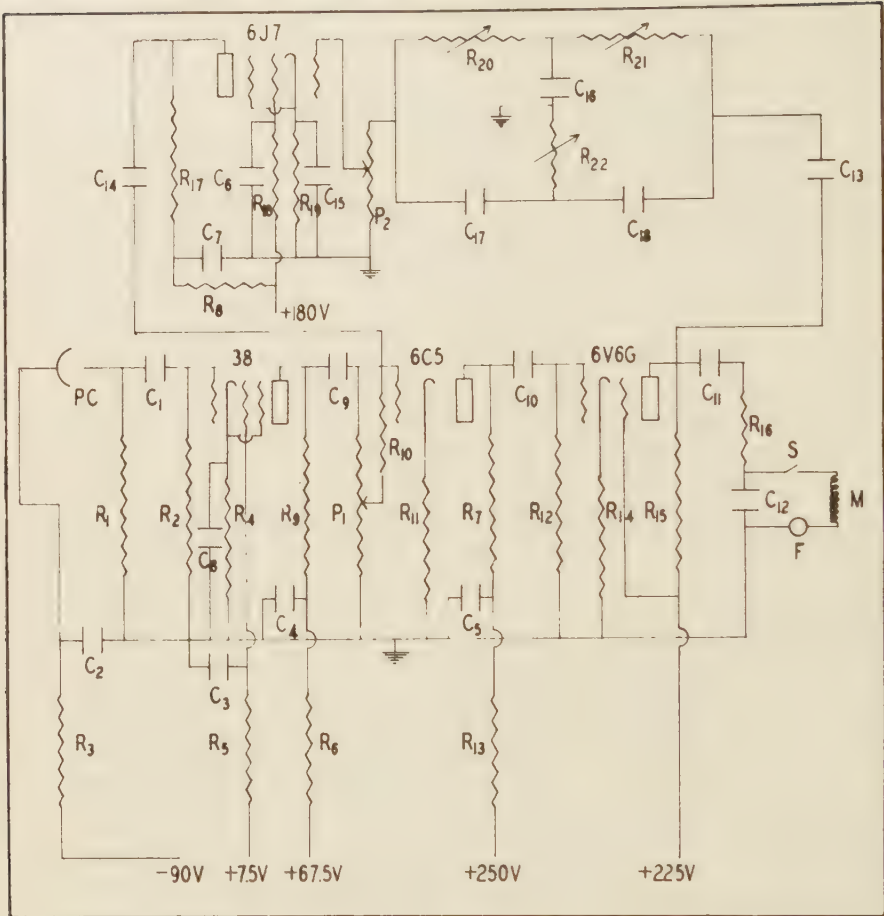


Fig. 3

capacities and resistances must be set carefully so that the bridge is accurately tuned to 60 cycles. The 6J7 serves to introduce an 180° phase shift in the output from the bridge. This is necessary because the feedback voltage which is taken off the plate of the last tube must have passed through an odd number of stages after having been introduced to the grid of the 6C5 and before re-entering it.

The amount of feedback voltage is varied by the gain con-

trol P_2 and is limited by the fact that the amplifier begins to oscillate and becomes unstable if too much gain is permitted. On the other hand, the selectivity of the amplifier depends on the value of the voltage being fed back through the degenerative network. One kind of oscillation, the frequency of which is close to 60 cycles, due partly to imperfect tuning of the bridge, can be greatly reduced by proper tuning and by omitting the cathode condenser of the 6V6G. All of the high frequency oscillations can be eliminated by the use of the condenser, C_{12} , placed across the output. The low frequency oscillations, which give the most trouble, can be reduced by omitting the cathode condensers from the last two stages and by employing as small a blocking condenser, C_{10} , as is feasible without sacrificing too much gain of the amplifier.

Generator Amplifier

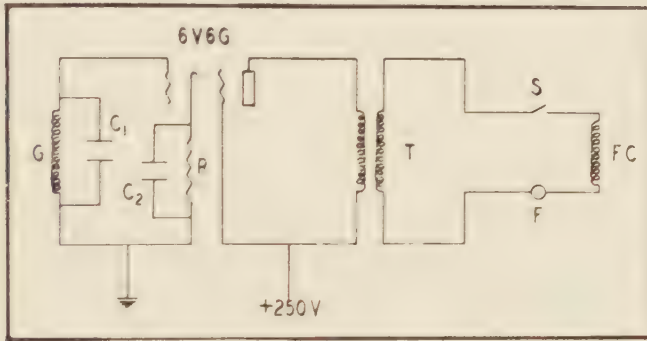


Fig. 4

- G - Generator coil
- C₁ - Paper condenser .25 microfarads
- C₂ - Electrolytic condenser 50 microfarads
- R - Carbon resistor 1500 ohms
- T - Thordarson transformer T-57S01
- S - Switch
- F - Fuse .1 ampere
- F.C. - Fixed coil of dynamometer

Fig. 4, above illustrates the one-stage amplifier used to amplify the voltage from the coil of the generator. A condenser placed across the coil of the generator greatly improves the wave form of the voltage being applied to the grid of the 6V6G. A

Thordarson universal output transformer is used to couple the tube to the fixed coil of the dynamometer.

The dynamometer used in connection with the amplifiers is a Leeds and Northrup astatic dynamometer No. 2450 with a current sensitivity of the instrument rated at 0.5 microampere per millimeter at one meter and the moving system damped by a vane in oil. In our work, the deflections on a zero-center, 200 centimeter scale were observed through a telescope with a scale to telescope distance of six meters.

The polarimeter, as described, can either be used as a null instrument or it can measure optical rotation in terms of dynamometer deflection. In the former case, one sets the analyzer in such a position that the deflection is zero. The optically active medium is then placed between the polarizer and analyzer and the latter is rotated until the reading is again zero; the rotation of the analyzer is that of the active medium. In the other method, the instrument is calibrated in terms of degrees of rotation per centimeter. After the analyzer has been set for zero reading, the deflection due to the optically active medium, gives the rotation.

Sources of Instability

Though, with the light source described above, we found that we could get a sensitivity of .001 degree rotation per centimeter, the instability of the instrument limited the reproducibility of readings to within a range of .02 degree. This was true even when it was only a matter of resetting the analyzer to the zero reading.

In our attempts to track down the main source of the instability, we obtained the following results. When the light is excluded from the photo-electric cell and the full gain of the amplifier is turned on, there is practically no deflection of the dynamometer and no instability. This is true even when four stages of amplification are used. The reason for this fortunate fact is that the moving coil in the dynamometer can receive a torque only when the input frequencies of the fixed coil and moving coil are the same. The output from the generator consists practically only of a 60 cycle component and its higher harmonics. The amount of noise from the other amplifier of these particular frequencies is so small that there is no deflection.

In the beginning of our work, the vibrations of the motor caused greater instability but after taking the measures described above to reduce vibrations, it was found that at the present stability, it is not the limiting factor. It was also suspected that because of the proximity of the coil of the generator to the motor, a 60 cycle voltage would be induced in it, due to the changing magnetic field from the motor. This was confirmed by noting that there was a voltage induced in the coil even when the latter was removed from the rest of the generator. However, it does not appear to be responsible for the observed fluctuations because it remains constant.

The fact that the fluctuations were comparatively slow and of the kind that one would expect from changes in light intensity from a source such as ours suggested that this might be the cause of the trouble. To test this assumption, a piece of microscope glass slide was placed before the analyzer and a deflection corresponding to a rotation of .3 degree was observed. Since the glass absorbs about 3% of the visible spectrum and the light source remains constant only to within .2% or .3%, it is seen that the fluctuations to be expected from the changes in light intensity are of the same order of magnitude as those actually observed. It must be remembered that this unsteadiness persists even when there is no deflection, i.e., the phase angle Θ is equal to $\frac{\pi}{2}$.

There are at least two possible explanations for the effect described above. Assuming that only the first and second harmonics from both amplifiers are effective, the deflection of the moving coil will be the sum of the torques resulting from the interaction of the two pairs of voltages of identical frequencies. If then, as is entirely possible, the percentage of the second harmonic from the amplifier, due to distortion in it, changes with a slight variation in light intensity, the reading on the dynamometer will be altered proportionally whether the original reading was that of the zero point of the dynamometer or not.

In order to decrease the amount of second and higher harmonics, the degenerative feedback circuit was added to the amplifier with the aid of which the amplitude of a 120 cycle input could be decreased by a factor of at least ten. Yet the decrease in the glass slide deflection, amounted to only about 15%. As was pointed out before, the amount of feedback voltage was limited and probably more improvement would result if additional feedback voltage could

be used. It appears, nevertheless, as though another factor is involved. From a consideration of the properties of vacuum tube circuits, this probably can be ascribed to a shift in the phase of the fundamental with a change in the percentage distortion.

Means of Improvement

The change in the instrument which would probably bring the greatest improvement, would be the construction of a linear amplifier. This would result in the reduction of the amount of second and higher harmonics and thereby decrease the change in the percentage of these harmonics when small light fluctuations occur. Another, perhaps more fruitful, consequence would be that the phase shift in the fundamental, due to changes in the percentage of distortion, would be diminished.

In order to employ more feedback voltage, it is necessary to prevent low frequency oscillations. This can be accomplished by employing a parallel resonance circuit with an air core inductance in the grid of the third stage. Another desirable change would be to increase the speed of the motor to twice its present value. Such a step would eliminate the effect on the deflection of voltages induced in the generator coil by the changing magnetic field of the motor.

To make this instrument adaptable to operation with low light intensities such as those from a monochromator, one need only add one or two more stages of amplification. It is very likely that no additional difficulties would appear because of the increased complexity of the amplifying circuit.

Trial Experiment

To test the polarimeter in actual use, determinations of the optical rotation of several unknown solutions of sucrose were made. White light from the light source described above was used in this experiment in order that there be a minimum of fluctuation in the light intensity.

The first step in the experiment was to calibrate the polarimeter in order to determine the sensitivity of the instrument and, in addition, to ascertain whether or not the deflection is a linear function of the rotation over the range under consideration. The calibration was carried out simply by noting the deflections

for different positions of the analyzer. Alternate readings with the light on and light off were made three times for each setting of the analyzer. Then the average deflection for each position of the analyzer was calculated. The results are plotted in the graph below, from which it can be seen that the dynamometer responds linearly to changes in the phase angle over the range of at least one degree. The sensitivity of the instrument for the setting of the gain used was .0089 degrees rotation per centimeter deflection.

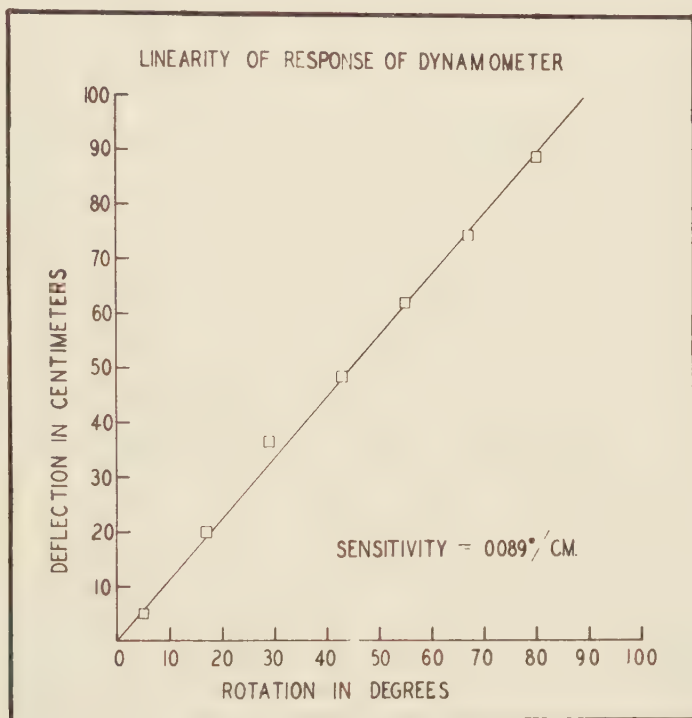


Fig. 5

Since white light was used in the experiment, it was necessary to determine the value of the specific rotation of the sugar for this wave length range. This was done by measuring the deflection of a solution of sucrose of known concentration by the same procedure as will be described for the unknown solution. Using the sensitivity, determined above, and the formula

$$[\alpha] = \frac{\alpha}{c \cdot l}$$

where $[\alpha]$ is the specific rotation, α the observed rotation, c the concentration in grams per c.c., l the length of the cell in decimeters, one can easily calculate the specific rotation. The value at the temperature of the experiment, 27.5°C , is 42.2° .

TABLE I

Conc. Grams/cc	D ₀	D	D ₀	Conc. Grams/cc	D ₀	D	D ₀
0.0000	- 7.8	11.4	- 6.8	0.0000	-19.2	0.3	-19.3
	- 6.8	11.8	- 7.5		-19.3	0.5	-19.7
	- 7.5	10.5	- 7.8		-19.7	0.3	-19.2
0.1044	-11.1	-42.2	-11.3	0.0021	-22.2	-10.7	-21.0
	-11.3	-41.7	-10.8		-21.0	- 9.8	-21.6
	-10.8	-43.0	-11.4		-21.6	-10.0	-20.0
0.0000	-12.2	7.0	-10.6	0.0010	-24.0	- 8.7	-25.0
	-10.6	7.7	-11.5		-25.0	- 9.0	-24.7
	-11.5	7.1	-12.0		-24.7	- 8.8	-24.5
0.0731	-14.5	-29.5	-14.7	0.0004	-25.0	- 5.8	-24.8
	-14.7	-29.4	-15.6		-24.8	- 5.9	-23.8
	-15.6	-29.2	-15.5		-23.8	- 5.8	-23.8
0.0522	-18.0	-21.5	-17.5	0.0000	-27.8	- 8.0	-28.5
	-17.5	-22.6	-18.5		-28.5	- 7.4	-27.5
	-18.5	-21.8	-17.3		-27.5	- 8.8	-29.0
0.0313	-18.0	-11.6	-17.0				
	-17.0	-11.8	-18.8				
	-18.8	-12.5	-18.1				

The procedure for determining the rotations of the unknown solutions is as follows. Cells one centimeter in length with windows of microscope glass slides were used. It was necessary to correct for the deflection, which occurs when the intensity of the light beam is decreased, due to absorption by the windows and solvent. This was done by observing the deflection when only pure solvent is used. Table I is a record of the readings as they were taken and indicates the reproducibility which can be obtained. For each solution there were three sets of three readings taken: the first and third readings, without the cell containing the solution, the second, with the cell. The first column in Table I indicates the grams of sucrose per c.c. of solution. D₀ is the scale reading without the solution and D with the solution. It is seen from

the table that the readings for any given solution fall within a range of two centimeters. It can also be noted from the increasing value of D_0 that there is a slow drift in the scale deflection.

TABLE II

Conc. Grams/cc	Average Deflection	Corrected Deflection	Observed Rotation	Calculated Rotation	Difference
0.0000	18.6	0.0			
0.1044	-31.2	-49.8	.443°	.441°	-.002°
0.0000	18.6	0.0			
0.0731	-14.2	-32.9	.293°	.308°	.015°
0.0522	- 4.1	-22.9	.204°	.220°	.016°
0.0313	6.3	-12.7	.113°	.132°	.019°
0.0000	19.1	0.0			
0.0021	10.7	- 8.7	.077°	.089°	.012°
0.0010	15.8	- 3.9	.035°	.042°	.007°
0.0004	18.5	- 1.6	.014°	.017°	.003°
0.0000	20.4	0.0			

In Table II is tabulated for each solution the average of three deflections, the average deflection corrected for absorption, and the observed and calculated rotations with their difference. The observed rotation is found by multiplying the corrected deflection by the sensitivity of the polarimeter. The calculated rotation is easily determined from the equation for the specific rotation by the use of the value of it determined above. From the figures in the difference column it can be seen that the maximum error in determining the rotation of a solution is .02°.

Conclusion

It has been demonstrated that in its present form the photo-electric polarimeter described above is accurate to .02°. In addition, definite recommendations for the improvement of the in-

strument have been made. In the opinion of the author, it should be possible to obtain an accuracy of the order of a few thousandths of a degree with the refinements suggested above. The instrument can readily be adapted to low light intensities by the addition of one or two more stages of amplification.

If the instrument is arranged to operate with low light intensities, then by rotation of the analyzer to a position of maximum deflection, i.e., the phase angle equal to 0, one can measure absorption coefficients by the same procedure used in ordinary photo-electric spectrophotometers.

